FORM PCT 1390 U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE REV 5/93	ATTORNEY'S DOCKET NO WOLF, D. ET AL-1 PCT
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371	U S APPLICATION NO. (if known, see 37 CFR 1 5) **09/786163**

INTERNATIONAL APPLICATION NO. PCT/DE99/02956	INTERNATIONAL FILING DATE 10 SEPTEMBER 1999	PRIORITY DATE CLAIMED 11 SEPTEMBER 1998

TITLE OF INVENTION
  METHOD FOR PRODUCING ACTION AND/OR SELECTIVE SOLID CATALYSTS FROM INORGANIC OR ORGANOMETALLIC MATERIALS

APPLICANT(S) FOR DO/EO/US
  DORIT WOLF ET AL

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. __X__ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.

2. ___ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.

3. __X__ This is an express request to begin national examination procedures (35 U.S.C. 371 (f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).

4. __X__ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.

5. __X__ A copy of the International Application as filed (35 U.S.C. 371(c)(2)
    a. __X__ is transmitted herewith (required only if not transmitted by the International Bureau)
    b. ____ has been transmitted by the International Bureau.
    c. ____ is not required, as the application was filed in the United States Receiving Office (RO/US).

6. __X__ A translation of the International Application into English (35 U.S.C. 371(c)(2)).

7. ____ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
    a. ____ are transmitted herewith (required only if not transmitted by the International Bureau).
    b. ____ have been transmitted by the International Bureau.
    c. ____ have not been made; however, the time limit for making such amendments has **NOT** expired.
    d. ____ have not been made and will not be made.

8. ____ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).

9. __X__ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).

10. ____ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. __X__ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.

12. __X__ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.

13. __X__ A **FIRST** preliminary amendment.
    ____ A **SECOND** or **SUBSEQUENT** preliminary amendment.

14. ____ A substitute specification.

15. ____ A change of power of attorney and/or address letter.

16. __X__ Other items or information:

      PCT/ISA/210 - Int'l. Search Report

Applicant Claims Priority under 35 U.S.C. §119 of __GERMANY__ Application No. _198 43 242.9_, Filed _11 SEPTEMBER 1998_
Applicant Claims Priority under 35 U.S.C. §120 of: PCT No. _PCT/DE99/02956_ filed _10 SEPTEMBER 1999_.

APPLICATION NO. (if known, see 37 CFR 1.5) **09/786163**	INTERNATIONAL APPLICATION NO PCT/DE99/02956	ATTORNEY'S DOCKET NO WOLF, D. ET AL-1

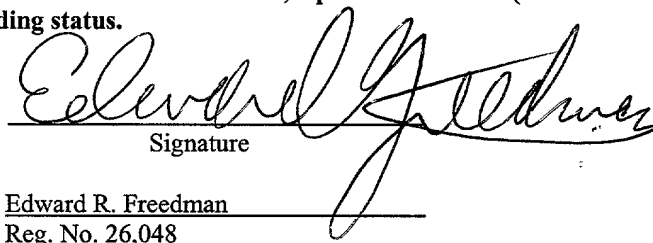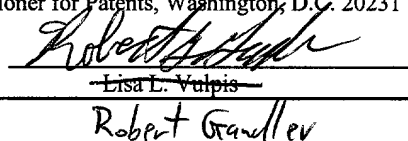|	CALCULATIONS	PTO USE ONLY
X The following fees are submitted: **Basic National Fee (37 CFR 1.492(a)(1)-(5)):** Search Report has been prepared by the EPO or JPO $860.00		
International preliminary examination fee paid to USPTO (37 CFR 1.482) $690.00		
Neither international preliminary examination fee paid (37 CFR 1.82) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO $1,000.00		
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4)...... ....$100 **ENTER APPROPRIATE BASIC FEE AMOUNT =**	$ 860.00	

Surcharge of **$130.00** for furnishing the oath or declaration later than ___ 20 ___ 30 months from the earliest claimed priority date (37 CFR 1 492(e)).

Claims	Number Filed	Number Extra	Rate		
Total Claims	15 - 20 =	- 0 -	X **$18.00**	$	
Independent Claims	1 - 3 =	- 0 -	X **$80.00**	$	
Multiple dependent claim(s) (if applicable)			+ **$270.00**	$	
TOTAL OF ABOVE CALCULATIONS =				$ 860.00	
Reduction by 1/2 for Small Entity status, if applicable.				$ 430.00	
SUBTOTAL =				$ 430.00	
Processing fee of **$130.00** for furnishing the English translation later than ___ 20 ___ 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +				$	
TOTAL NATIONAL FEE =				$ 430.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)) The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3 31). **$40.00** per property +				See cover sheet attached to assign $ to be charged to Deposit Acct	
TOTAL FEES ENCLOSED =				$ 430.00	
				Amount to be: refunded	$
				charged	$

X Applicant claims Small Entity status.
a. **X** A check in the amount of $ 430.00 to cover the above fees is enclosed.
b. ___ Please charge my Deposit Account No. 03-2468 in the amount of $_____ to cover the above fees. A duplicate copy of this sheet is enclosed.
c. **X** The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment, to Deposit Account No. 03-2468. A duplicate copy of this sheet is enclosed.
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:
COLLARD & ROE, P.C.
1077 Northern Boulevard
Roslyn, New York 11576-1696
(516) 365-9802

_____
Signature

Edward R. Freedman
Reg. No. 26,048

Express Mail No. EL 622 001 327 US
Date of Deposit February 28, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10, on the date indicated above, and is addressed to the Ass't. Commissioner for Patents, Washington, D.C. 20231

Lisa L. Vulpis

Robert Grandler

R:\Vita\Ingrid\Wolf, D et al-1 PCT transm wpd

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

U.S. National Stage Patent Application of

APPLICANT: DORIT WOLF ET AL

PCT NO.:   PCT/DE99/02956   PCT FILED: 10 SEPTEMBER 1999

PRIORITY: 198 43 242.9   PRIORITY FILED: 11 SEPTEMBER 1998

TITLE: METHOD FOR PRODUCING ACTION AND/OR SELECTIVE SOLID
               CATALYSTS FROM INORGANIC OR ORGANOMETALLIC MATERIALS

PRELIMINARY AMENDMENT

ATTN.: BOX PCT APPLICATION
Asst. Commissioner for Patents
Washington, D.C. 20231

Dear Sir:

Preliminary to examination, please amend the above-identified

U.S. national stage patent application as follows:

IN THE SPECIFICATION:

On page 1, after line 32 (as marked on the left margin),

please insert the following paragraph:

--From Advances in Catalysis 2 (1950) 81-104 an empirical

search of promoters for inorganic multi-substance catalysts is

known. In EP-A-0589384 an iterative method for the determination

of parameter values is described in which the optimization strategy

-1-

resides in that a binary string is attached to the number of

experiments per plane, these are exchanged sequentially with steped

probability, and then changed to real values.--

IN THE CLAIMS:

Please cancel claim 1 and insert new claim 16 attached hereto.

In claim 2, line 2, change "1" to --16--;

line 114 (i.e., first line of (i) on claim page 5), before

"n-th" insert --first to--;

line 120, (i.e., line 6 of (i)), delete ",";

line 123, (i.e., line 1 of (j)), delete "comments";

In claim 5, line 1, delete "(a)".

In claim 15, line 1, change "1" to --16--.

line 3, cancel "according to claim 11, 12, and 13,".

Please add an Abstract of the Disclosure on its own separate
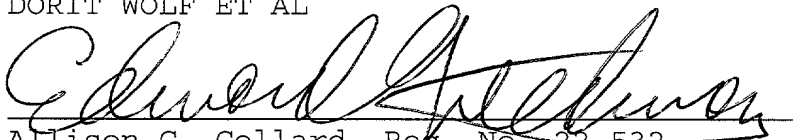
page attached hereto.

REMARKS

By this Preliminary Amendment, a discussion of a prior art reference has been inserted into the specification. Claim 1 has been replaced by new claim 16 and miner changes have been made in claim 2. Claims 2 and 15 have also been amended to make them properly dependent on new claim 16. In addition, an Abstract of the Disclosure is being provided. The amendments correspond to amendments in the international application, and no new matter has been introduced.

Entry of this amendment is respectfully requested.

Respectfully submitted,

DORIT WOLF ET AL

Allison C. Collard, Reg. No. 22,532
Edward R. Freedman, Reg. No. 26,048
COLLARD & ROE, P.C.
Attorneys for Applicants

1077 Northern Boulevard
Roslyn, New York 11576
(516) 365-9802
Enclosures: Abstract, claim 16

Lisa L. Vulpis
Robert G. Goodler

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-3-

16. A method for preparing active or selective solid
    catalysts of inorganic or organometallic materials or
    mixtures thereof by selecting a certain number of solid
    catalysts of different chemical composition or different
    weight composition or different chemical and different
    weight composition and determination of essential
    catalyst properties, comprising arbitrarily or randomly
    newly structuring by means of crossing and mutation,
    selected among the stochastic methods of random-check
    generators, throwing dice, and/or performing drawings,
    the individual catalyst components or amounts of mass of
    the catalyst components or the catalyst components and
    amounts of mass in the best catalysts of the first
    generation, in the form of certain chemical compounds,
    with respect to activity or selectivity or activity and
    selectivity for a certain catalytic reaction,
    determining the activity or selectivity or activity and
    selectivity of the obtained catalysts of the second
    generation,
    again arbitrarily or randomly newly structuring by means
    of the aforementioned stochastic methods the individual
    catalyst components or amounts of mass of the catalyst
    components or the catalyst components and amounts of
    mass of a portion of the best catalysts of the second
    generation,
    determining the activity or selectivity or activity and
    selectivity of the obtained catalysts of the third
    generation, and continuing these steps of new
    structuring of the best catalysts of all generations and
    the property determination up to obtaining one or more
    catalysts with the desired properties for the specific
    catalytic reaction.

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANTS: WOLF ET AL
SERIAL NO.:   09/786,163   EXAMINER:
FILED: FEBRUARY 28, 2001   GROUP:
INT'L. APPLN. NO.: PCT/DE99/02956   FILED: 10 SEPTEMBER 1999
FOR: METHOD FOR PRODUCING ACTION AND/OR SELECTIVE SOLID
         CATALYSTS FROM INORGANIC...

SECOND PRELIMINARY AMENDMENT

ATTN: BOX PCT
Assistant Commissioner of Patents
Washington, D.C. 20231

Dear Sir:

     Preliminary to the initial Office Action, please amend the
above-identified application as follows:

IN THE SPECIFICATION:

     Please cancel Page 1 and replace with new Pages 1 and 1a,
attached hereto as Exhibit A.

REMARKS

     By this Second Preliminary Amendment, the application has
been amended to conform with U.S. practice, page 1 has been
substituted by new pages 1 and 1a to show the cross-reference to
related applications. No new matter has been introduced. Entry
of this Amendment is respectfully requested.

                              Respectfully submitted,
                              DORIT WOLF ET AL

COLLARD & ROE, P.C.   Allison C. Collard, Reg. No.22,532
1077 Northern Boulevard   Edward R. Freedman, Reg. No.26,048
Roslyn, New York 11576   Attorneys for Applicant
(516) 365-9802

Enclosures: Exhibit A, new pages 1 and 1a

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Date of Deposit: APRIL 10, 2001

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under 37 C.F.R. 1.10, on the date indicated above, and is addressed to the Commissioner of Patents and Trademarks, Washington, D.C. 20231.
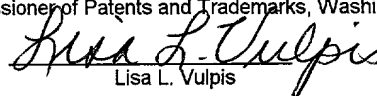
                                   Lisa L. Vulpis

EXHIBIT A

METHOD FOR PRODUCING ACTIVE AND/OR SELECTIVE SOLID CATALYSTS FROM INORGANIC OR ORGANOMETALLIC MATERIALS

CROSS REFERENCE TO RELATED APPLICATIONS

Applicants claim priority under 35 U.S.C. §119 of GERMAN Application No. 198 43 242.9 filed 11 SEPTEMBER 1998. Applicants also claim priority under 35 U.S.C. §120 of PCT/DE99/02956 filed on 10 SEPTEMBER 1999. The international application under PCT article 21 (2) was not published in English.

The invention relates to a method for a fast and economic development of solid catalysts for heterogeneous catalytic reactions, occurring in processes in the chemical production and in the refinery technology as well as in environmental technology, by their parallel testing according to evolutionary methods.

The new development or improvement of heterogeneous inorganic solid catalysts is based on empirical expert knowledge and basic knowledge. Even though a comprehensive basic knowledge is available in regard to the function of individual inorganic components or compounds in the catalysis of certain partial reaction steps, which is of decisive importance for the catalyst development, it cannot be avoided in practice within the near future to prepare a large number of catalysts which are comprised of different active components or phases and to test them with regard to the catalytic action for the reaction in consideration.

For carrying out a predetermined reaction, several catalytically active phases will generally be available which are produced in a suitable manner and in a ratio of the active components to be empirically determined and which are combined in this way. The knowledge of physical, physical-chemical, and catalytic properties

-1-

of solid bodies forms a rational basis for the selection of
catalytically active materials in the catalyst development and
improvement. Even when in an ideal situation the correct individual
components or individual phases of the catalyst can be selected, it
is required to determine the suitable mass ratio and preparation
method.

From Advances in Catalysis 2 (1950) 81-104 an empirical search of
promoters for inorganic multi-substance catalysts is known. In EP-
A-0589384 an iterative method for the determination of parameter
values is described in which the optimization strategy resides in
that a binary string is attached to the number of experiments per
plane, these are exchanged sequentially with steped probability,
and then changed to real values.

A suitable method for such optimization problems is the application
of combinatorial and evolutionary methods (Ugi, I. et al., Chimia
51 (1997) 39 - 44). These algorithms have been employed in the past
in biochemistry and active ingredient research in order to select
within a time as short as possible new substances with a desired
specific activity from a plurality of compounds. These principles
have also been used in

-1a-

Method For Producing Active And/Or Selective Solid Catalysts From Inorganic Or Organometallic Materials

The invention relates to a method for a fast and economic
5 development of solid catalysts for heterogeneous catalytic
reactions, occurring in processes in the chemical production
and in the refinery technology as well as in environmental
technology, by their parallel testing according to
evolutionary methods.

10 The new development or improvement of heterogeneous
inorganic solid catalysts is based on empirical expert
knowledge and basic knowledge. Even though a comprehensive
basic knowledge is available in regard to the function of
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20 catalytic action for the reaction in consideration.

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active components to be empirically determined and which are
25 combined in this way. The knowledge of physical, physical-
chemical, and catalytic properties of solid bodies forms a
rational basis for the selection of catalytically active
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when in an ideal situation the correct individual components
30 or individual phases of the catalyst can be selected, it is
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method.

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application of combinatorial and evolutionary methods (Ugi,
35 I. et al., Chimia 51 (1997) 39 - 44). These algorithms have
been employed in the past in biochemistry and active ingredient
research in order to select within a time as short as possible
new substances with a desired specific activity from a
plurality of compounds. These principles have also been used in

the meantime in the development of homogenous catalysts (DE-A 197319904). In the aforementioned applications the substances to be examined are always in solution. The activity range of the desired property (e.g., catalytic activity and selectivity)

5   is limited to a molecule whose optimal element composition and structure is to be found.

In contrast to this, in the heterogeneous catalysis the object is to select the catalytically most effective inorganic solid materials and to determine their optimal weight

10   proportion in the final catalyst. By application of new strategies in the development of heterogeneous catalysts, the experimental expenditure in the catalyst development is to be reduced, on the one hand, and the probability of finding an optimal catalyst is to be increased, on the other hand, in

15   comparison to the currently still substantially empirically oriented methods employed in practice.

The combinatorial approach is an effective developmental strategy when a large number of parameters affect the properties of products. Despite the great success of this

20   strategy in the development of new medicaments, the application of combinatorial methods in the inorganic chemistry and catalysis is a new field. The first application of combinatorial methods in the development of new solid materials was reported in the year 1995 by Schultz et al., Science, **268**

25   (1995) 1738 and Science **270** (1995) 273. The authors have demonstrated that the solid material libraries can be tested with respect to superconductivity and magneto resistance. In the same year, libraries of complexes for the selective bonding of metal ions as well as of phosphine-containing peptide

30   ligands for the Rh(I)-catalyzed hydrogenation of methyl-2-acetamido acrylate to N-acetyl alanine methyl ether were established.

The synthesis of libraries containing a large number (up to 26,000) of combinations of inorganic materials on a silicon

35   matrix has been described (E. Danielson et al., Nature **389** (1997) 944). This technology was tested, inter alia, on the example of heterogeneous catalytic CO oxidation for determining analytically active solid materials. The obtained results were represented in three-dimensional diagrams from which the

combinations which resulted in high CO_2 yields and thus an increased catalytic activity could be determined.

Moreover, a synthesis of a library of polyoxy metallates with Keggin structure have been described (C.L. Hill et al., J. Mol. Catal. A **114** (1996) 114); 39 homogeneously dissolved catalysts were prepared by mixing aqueous solutions of $Na_2MO_4 \cdot 2H_2O$, $NaVO_3$ und Na_2MPO_4 (M = W, Mo). The resulting solutions were used without further treatments in the aerobic oxidation of tetrahydro thiophen to sulfoxide at 95°. The educt conversion and the product formation were determined by means of the GLC analysis and presented as a three-dimensional ※reaction histogram※ (x-axis - Mo/W content; y axis - V content; z axis - product yield). Since with most catalysts comparable results were obtained, no sound conclusion could be drawn.

A combinatorial strategy has been used by Mallouk et al. (Fuel Cell Seminar: Orlando, Florida (1996) 686) in the development and optimization of alloys of three metals which are used as anode materials in the electrochemical oxidation of methanol. For the preparation of libraries (9 arrays with 135 compositions) five noble metals (Pt, Ru, Os, Rh, and Pd) were used. This work is an example for an effective parallel testing.

Combinatorial libraries of metal catalysts supported on Al_2O_3 (inter alia Bi, Cr, Co, Cu, Ni, Pd) with 16 elements of a matrix are used by Willson et al. in the hydrogen oxidation reaction. The reactor was furnished with a special camera for the in-situ IR thermography; the catalytic activity was therefore determined via the ignition temperature. A disadvantage of the analytical method employed in this work is that the information in regard to product selectivity is missing.

In the above described methods of a combinatorial approach and their use for determining active compounds and optimized catalysts, very many syntheses for these target materials are performed which are time-consuming and material-intensive.

It is therefore an object of the invention to develop a method for preparing heterogeneous solid catalysts for a

predetermined reaction with reduced expenditure wherein the combinatorial approaches are supplemented or replaced by other optimization methods.

According to the invention evolutionary principles such as crossing and mutation are used and, in this connection, a stochastic modification of the catalyst composition is employed. These methods do not lead to a pure random search but, by an activity and selectivity determined selection of the catalysts to be modified, to a directed optimization which focuses quickly and parallel on several promising areas of the catalysts composition.

According to the invention the following procedure is followed:

(i) preparing substance libraries of individual catalytic materials and their mixtures,

(ii) testing of materials, i.e., individual materials and their mixtures of these substance libraries, with regard to their catalytic activity,

(iii) determining the chemical structure of the catalytically active materials,

(iv) carrying out an iterative repetition of the steps (i) to (iii) or also (iv), based on the results obtained according to (ii) and (iii), with the goal of catalyst optimization.

This procedure can be realized or practically applied in the development of heterogeneous catalysts as follows:

In the first step (i) primary components (individual materials or catalytically active phases), which have already been described or are known or have been determined empirically or intuitively for the individual reactions steps of the heterogeneous catalytic reaction under consideration, are selected and introduced into the substance library; wherein by a random selection arbitrary mixtures of these individual materials are produced. In the second step (ii) these materials finally determined and prepared in this way (first generation of catalysts) are catalytically tested (for example, activity, selectivity, space-time yield); these two procedures, i.e., preparation and testing, are performed parallel as much as possible, respectively. The successful materials with respect to catalysts optimization of the step (ii) are physically and

physical-chemically characterized in particular with respect to their reproducible preparation in step (iii) and present the foundation for the subsequent second generation of catalysts. This second generation is generated according to methods of biological evolution from the successful materials of the first generation and then subjected to the steps (ii) and (iii).

Methods of biological evolution in this context are to be understood as crossing and mutation. In this connection, by means of stochastic methods, such as a random-check generators, throwing dice, drawing, a change of catalyst components and/or weight proportions of one or more catalysts of a selected pool of catalysts of the previous generation is performed by an arbitrary and/or random new structuring.

In the second and the subsequent iterations, the most successful catalysts of all generations are employed as a foundation, respectively, whose total number relative to the total number of catalysts of a generation, however, is generally small. In general, it will be 1 to 50 % of the catalysts of one generation.

The described iterations are performed until no improvement of the catalytic behavior of the materials with respect to activity and/or selectivity for the reaction under consideration can be determined anymore.

The method for selecting components for the preparation of active and/or selective solid catalysts of inorganic or organometallic materials or mixtures thereof is comprised advantageously of the following steps, in which

(a) for a catalytic reaction a number n_1 of solid catalysts of the elements of the periodic table of the elements (PTE) in the form of compounds of the formula (I)

$$\left(A_{a_1}^1 .. A_{a_i}^i\right) - \left(B_{b_1}^1 .. B_{b_j}^j\right) - \left(D_{d_1}^1 .. D_{d_k}^k\right) - \left(T_{t_1}^1 .. T_{t_l}^l\right) - O_p \qquad (I)$$

are prepared, wherein $A^1 .. A^i$ are i different main components which are selected from the elements of the PTE, except trans uranium and noble gas elements, preferably of the group

Mg, Ca, Sr, Ba, Y, La, Ti, Zr, V, Nb, Cr, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, B, Al, Ga, In, C, Si, Sn, Pb, N, P, As, Sb, Bi, S, Se, Te, F, Cl, Ce and Nd and the number i is between 1 and 10,

B^1 .. B^j are j different minor components selected from the group of the elements

Li, Na, Ka, Mg, Ca, Sr, Ba, Y, La, Ti, Zr, V, Nb, Cr, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, B, Al, Ga, In, C, Si, Sn, Pb, N, P, As, Sb, Bi, S, Se, Te, F, Cl, Ce and Nd and the number j is between 1 and 10,

D^1 .. D^k are k different doping elements which are selected from the group of the elements

Li, Na, Ka, Mg, Ca, Sr, Ba, Y, La, Ti, Zr, V, Nb, Cr, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, B, Al, Ga, In, Si, Sn, Pb, N, P, As, Sb, Bi, S, Se, Te, F, Cl, Ce and Nd and the number k is between 1 and 10,

T^1 .. T^l are l different support components which are comprised of oxides, carbonates, carbides, nitrides, borides of the elements Mg, Ca, Sr, Ba, La, Zr, Ce, Al, Si or a mixed phase of two or more thereof, and the number l is between 1 and 10, and O is oxygen,

a_1..a_i are identical or different mole fractions of 0 to 100 mole-% with the provision that the mole fractions a_1..a_i cannot all at the same time be 0,

b_1 .. b_j are mole fractions of 0 to 90 mole-%, preferably 0 to 50 mole-%,

d_1 .. d_k are mole fractions of 0 to 10 mole-%,

t_1 .. t_l are mole fractions of 0 bis 99.99 mole-%,

p is a mole fraction of 0 to 75 mole-%, wherein the sum of all mole fractions a_i + b_j + d_k + t_l may be not greater than 100 %, and

the number n_1 of catalysts with different quantitate composition and/or different chemical composition is in the range of 5 to 100,000, preferably in the range of 5 to 100;

(b) the activity and/or selectivity of the n_1 solid catalysts prepared according to (a) of the first generation is determined experimentally for a catalytic reaction in a reactor or in several reactors switched parallel;

(c) a number of 1 - 50 % is selected as number n_2 from the number n_1 of the catalysts of the first generation having the highest activities for a specific reaction and/or highest selectivities for the desired product or product mixture of the catalytic reaction;

(d) the catalyst components contained in the number n_2 of the catalysts with a pre-set probability W, which results for each of the components A^1 .. A^i, B^1 .. B^j, D^1 .. D^k and T^1 .. T^l from the corresponding equations

$$W_A = \frac{1}{i \cdot n_2} \cdot 100\%, W_B = \frac{1}{j \cdot n_2} \cdot 100\%, W_D = \frac{1}{k \cdot n_2} \cdot 100\%, W_T = \frac{1}{l \cdot n_2} \cdot 100\%$$

are exchanged between two catalysts selected from the number n_2 with a probability of $W_{cat} = \frac{1}{n_2} \cdot 100\%$ and/or that the amount of mass a_1 .. a_i, b_1 .. b_j, d_1 .. d_k and t_1 .. t_l of the catalyst components A^1 .. A^i, B^1 .. B^j, D^1 .. D^k and T^1 .. T^l for some of the catalysts selected with a probability of $W_{cat} = \frac{1}{n_2} \cdot 100\%$ are varied in that new values for the mole fractions a_1 .. a_i, b_1 .. b_j, d_1 .. d_k and t_1 .. t_l are determined within the limits defined under (a);

in this way new catalysts of the general formula (I) with the meaning of A^1 .. A^i, B^1 .. B^j, D^1 .. D^k, T^1 .. T^l, a_1 .. a_i, b_1 .. b_j, d_1 .. d_k and t_1 .. t_l and p defined under (a) are produced in a number y_2 which form the catalysts of the second generation;

(e) the activities and/or selectivities of the y_2 solid catalysts of the second generation are determined experimentally for the same specific reaction as in (b) in one or more reactors;

(f) a number of the n_3 catalysts of the second generation, having the highest activities for a specific reaction and/or highest selectivities for the desired product and product mixture of all solid catalysts of the first and second generation, is selected, wherein the number n_3 is 1 to 50 % of the number n_1;

(g) the catalyst components contained in the number n_3 of the catalysts with a pre-set probability W, which results for each of the components A^1 .. A^i, B^1 .. B^j, D^1 .. D^k and T^1 .. T^l from the corresponding equations

$$W_A = \frac{1}{i \cdot n_3} \cdot 100\%, W_B = \frac{1}{j \cdot n_3} \cdot 100\%, W_D = \frac{1}{k \cdot n_3} \cdot 100\%, W_T = \frac{1}{l \cdot n_3} \cdot 100\%$$

are exchanged between two catalysts selected from the number n_3 with a probability of $W_{cat} = \frac{1}{n_3} \cdot 100\%$ and/or that the amount of mass $a_1 \ .. \ a_i$, $b_1 \ .. \ b_j$, $d_1 \ .. \ d_k$ and $t_1 \ .. \ t_l$ of the catalyst components $A^1 \ .. \ A^i$, $B^1 \ .. \ B^j$, $D^1 \ .. \ D^k$ and $T^1 \ .. \ T^l$ for some of the catalysts selected with a probability of $W_{cat} = \frac{1}{n_3} \cdot 100\%$ are varied in that new values for the mole fractions $a_1 \ .. \ a_i$, $b_1 \ .. \ b_j$, $d_1 \ .. \ d_k$ and $t_1 \ .. \ t_l$ are determined within the limits defined under (a);

in this way new catalysts of the general formula (I) with the meaning of $A^1 \ .. \ A^i$, $B^1 \ .. \ B^j$, $D^1 \ .. \ D^k$, $T^1 \ .. \ T^l$, $a_1 \ .. \ a_i$, $b_1 \ .. \ b_j$, $d_1 \ .. \ d_k$ and $t_1 \ .. \ t_l$ and p defined under (a) are produced in a number y_3 which form the catalysts of the third generation;

(h) the activity and/or selectivity is of the y_3 new solid catalysts of the third generation prepared according to (g) is determined experimentally for the same specific reaction as in (b) in one or more reactors;

(i) a number of n_{n+1} solid catalysts of the n-th generation, having the highest activities for a catalytic conversion and/or the highest selectivities for the desired product and product mixture of all solid catalysts of the first to n-th generation, is selected, wherein the number n_{n+1} is 1 to 50 % of the number n_1;

(j) the catalyst components contained in the number n_{n+1} of the catalysts with a pre-set probability W, which results for each of the components $A^1 \ .. \ A^i$, $B^1 \ .. \ B^j$, $D^1 \ .. \ D^k$ and $T^1 \ .. \ T^l$ from the corresponding equations

$$W_A = \frac{1}{i \cdot n_{n+1}} \cdot 100\%, W_B = \frac{1}{j \cdot n_{n+1}} \cdot 100\%, W_D = \frac{1}{k \cdot n_{n+1}} \cdot 100\%, W_T = \frac{1}{l \cdot n_{n+1}} \cdot 100\%$$

are exchanged between two catalysts selected from the number n_{n+1} with a probability of $W_{cat} = \frac{1}{n_{n+1}} \cdot 100\%$ and/or that the amount of mass $a_1 \ .. \ a_i$, $b_1 \ .. \ b_j$, $d_1 \ .. \ d_k$ and $t_1 \ .. \ t_l$ of the catalyst components $A^1 \ .. \ A^i$, $B^1 \ .. \ B^j$, $D^1 \ .. \ D^k$ and $T^1 \ .. \ T^l$ for some of the catalysts selected with a probability of $W_{cat} = \frac{1}{n_{n+1}} \cdot 100\%$ are varied in that new values for the mole

fractions a_1 .. a_i, b_1 .. b_j, d_1 .. d_k and t_1 .. t_l are determined within the limits defined under (a);

in this way new catalysts of the general formula (I) with the meaning of A^1 .. A^i, B^1 .. B^j, D^1 .. D^k, T^1 .. T^l, a_1 .. a_i, b_1 .. b_j, d_1 .. d_k and t_1 .. t_l and p defined under (a) are produced in a number y_{n+1} which form the catalysts of the (n+1)-th generation;

(k) the activity and/or selectivity is of the y_{n+1} solid catalysts of the (n+1)-th generation prepared according to (g) is determined experimentally for the same specific reaction as in (b) in one or more reactors;

(l) the selection according to the steps (c) + (f) + (i), the preparation of a new catalyst generation according to the steps (d), (g), (j), and the activity/selectivity determination according to the steps (e) + (h) + (k) is continued up to obtaining a catalyst generation in which the activity and/or selectivity relative to the previous generations as an arithmetic mean is not increased or no longer significantly increased (>1 %).

The selection number n_2, n_3, or n_{n+1} corresponds preferably to 5 to 30 % of the number n_1.

The exchange of the catalysts for the variation of the amount of mass or exchange and variation in the steps (d), (g), and (j) is performed preferably by means of a numerical random-check generator. In this connection, advantageously the program codes G05CAF, G05DYF, G05DZF oder G05CCF of the NAG Library (NAG FORTRAN Workstation Library, NAG Group Ltd., 1986) of a numerical random-check generator are used.

However, it is also possible to employ random-check generators which are available freely on the Internet or which are commercially available as software such as "Numerical Recipes in FORTRAN, PASCAL oder C", Cambridge University Press, or IMSL Libraries of the FORTRAN compilers DIGITAL visual Fortran Professional Edition.

Other stochastic methods such as rolling the dice or drawings can also be used for this step.

When employing such methods, in the step (d) several catalyst components can be selected and their corresponding mole fractions can be exchanged between the previously selected

catalyst components (crossing). Accordingly, it is also possible to effect via the molar fractions, which are changed from a finite value to zero or from zero to a finite value, an exchange of the individual catalyst components themselves by means of crossing so that overall a new composition of the catalyst of the new generation is obtained. However, it is also possible to reduce or enlarge (mutation) the catalyst components selected, for example, by means of random-check generator, by multiplication with factors which are determined randomly or freely selectable from the set of real numbers between 0 and 10,000 so that the new catalyst of the next catalyst generation contains the same components but in different concentrations so that also the ratios of the components relative to one another can be changed.

In the method step (a) the number n_1 of catalysts having different weight composition and/or different chemical composition is in the range of 5 to 100.

Advantageously, the preparation of the catalyst mixtures is carried out by mixing salt solutions of the elements of the component A^1 .. A^i, B^1 .. B^j, D^1 .. D^k and T^1 .. T^l and a subsequent thermal treatment in the presence of a reactive or inert gas phase (in the following referred to as tempering) or by common precipitation of sparingly soluble compounds and subsequent tempering or by loading the support components T^1 .. T^l with salt solutions or gaseous compounds of the components A^1 .. A^i, B^1 .. B^j, D^1 .. D^k and subsequent tempering, wherein the employed salts may be nitrates, sulfates, phosphates, carbonates, halogenides, oxalates, carboxylates or mixtures thereof or carbonyl compounds or acetyl acetonates.

The preparation of new catalyst mixtures of the second to n-th generation can be realized by mechanically mixing the prepared solid catalyst of the respective previous generations. Further advantageous embodiments reside in that the catalytic reaction is performed with liquid, vaporized, or gaseous reactants and that the reactants for the catalytic reaction are supplied to several reactors, and the product stream exiting from the reactors is analyzed separately for each individual reactor.

For performing the catalytic reaction, preferably 5 to 1,000 reactors, comprised of spaces with catalytically active material arranged therein, are switched parallel to one another or arranged in arrays, wherein the diameter of the spaces is 5 100 μm to 10 mm and the lengths are 1 mm to 100 mm. The throughput of the reactants is selected for a predetermined reactor length such that the desired conversion rate is achieved.

The reactor can be realized by a monolithic block with 10 many parallel channels, wherein the channels can be closed the inlet or outlet side individually or in a larger number also during the catalytic reaction, or by a porous module, preferably with channels extending parallel to the flow direction of the reaction mixture, which channels can be closed 15 selectively at the inlet or outlet side individually or in a larger number also during the catalytic reaction.

Advantageously, the reactants are supplied for the catalytic reaction to the above reactors and the composition of the product streams exiting the reactors are analyzed by a 20 measuring sensor wherein the measuring sensor is guided two-dimensionally across the outlet cross-sections of all reactors or the reactors are moved two-dimensionally relative to the measuring sensor and the portion of the product streams received by the measuring sensor is supplied to the analytical 25 device. The analytical device can be a gaschromatograph, a mass spectrometer, or another device for the analysis of gas or liquid mixtures.

The reaction mixture can have added thereto suitable indicators which indicate the presence of individual or several 30 educts or products and thus make possible their analysis in the reactant mixture. The preparation of the solid catalysts can be realized from solids, solutions, or dispersions.

The term ⊠catalyst improved in regard to activity or selectivity⊠ means that the catalysts with respect to their 35 activity or selectivity or with respect to both properties shows improved values. This compares to the improvement of the space/time yield.

The term ✕stochastic method✕ includes all not strictly deterministic processes with a random component. The stochastic methods of the invention are finite or discrete methods.

The invention will be explained with the aid of the attached drawing. It is shown in:

Fig. 1 a diagram showing the change of yield of the respectively best five catalysts during the first three generations of catalyst optimization according to example 1;

Fig. 2 a diagram as in Fig. 1 according to example 2.

The invention will be explained with the following examples. Example 1 concerns the search for an optimized catalyst for the partial oxidation of propane to its oxygen derivatives which encompasses the sum of acrolein, acetic acid, and acrylic acid.

Example 1

The selection and mixture of individual catalyst components which are divided into main, minor, doping, and support components as well as the testing and further improvement of the catalyst mixtures with application of evolutionary optimization strategies is demonstrated.

First 30 catalysts (phase I), subsequently 10 catalysts (phase II), and then further 10 catalysts (phase III), comprised of main components, minor components, doping components, and support material are prepared with the goal of convert propane to its oxygen derivatives by oxidation with oxygen and to minimize the resulting oxides CO and CO_2 (compare step (a) above). The course of the process comprises the following steps and leads to the respective denoted results.

1. Catalyst Generation

Step 1. The main components are selected from the oxides of the elements V, Mo, Nb, Bi, P. The proportion of the main components are varied between 0 and 50 mole-%. The minor components are selected from the oxides of the elements Mn, Sb, Sn, and B. The proportions of the minor components are varied between 0 and 50 mole-%. The doping components are selected from the oxides of the elements Cs and either Fe or Co, either Ag or Cu, and either Ga or In. The proportions of the doping components are varied between 0 and 5 mole-%. As a further

doping component Pd was used which was either not introduced or introduced in an amount of 10^{-4} mole-%. As a support component Al_2O_3 was provided which was either not present or present in an amount of 50 % by weight in the catalyst.

5   The sum of all weight or mole ratios of the main, minor, and doping and support components yields always 100 %.

Step 2. The catalysts which were used for testing, were obtained according to the following manufacturing process. Compounds (oxides, oxalates, or nitrates) of the elements mentioned in step 1 were dissolved in a little water or suspended, mixed with one another, and the mixture was evaporated. The resulting solid material was dried for 1 hr. at 200 °C and 3 hrs. at 400 °C, subsequently ground intensively for 1 hr. in a ball mill and tempered for 3 hrs. at 600 °C in air.

Step 3. The catalysts compositions of the first generation obtained by the random-checked generators G05DZF, G05CAF, G05DYF und G05CCF of the NAG-Bibliothek (NAG FORTRAN Workstation Library, NAG Group Ltd., 1986) are compiled in Table 1.

Step 4. The testing of the catalysts is carried out parallel in six quartz reactors (inner diameter 6 mm) which are introduced into the heatable and coolable fluidized sand bed for temperature control. Alternative configurations of the parallel testing of the solid catalysts are possible according to the above description.

The following standard conditions were selected for the testing of the catalysts: $T = 500$ °C, $m_{catalyst} = 1,0$ g, $\dot{V}_{total}$ per reactor = 28 ml_{STP} min^{-1} mit $\dot{V}_{C3H8} = 0.8$ ml_{STP} min^{-1}, $\dot{V}_{O2} = 5.6$ ml_{STP} min^{-1}, $\dot{V}_{H2O} = 12,0$ $ml_{STP}min^{-1}$, $\dot{V}_{Ar} = 21,6$ ml_{STP} min^{-1}.

The catalysts were used for the reaction and tested with respect to the sum of the yields of acrolein and acrylic acid obtained under the standard experimental conditions (compare step (b) above; corresponds also to this step in claim 2). The concentration of propane, propene, ethylene, the resulting oxygen derivatives as well as of CO and CO_2 was analyzed by means of a gaschromatograph and mass spectrometer.

Step 5. The results of the test of the first generation of catalysts are compiled in the form of the sum of the yield of acrolein and acrylic acid in Table 1. Significant differences in the yields of the 30 tested catalysts result. The best five catalysts (Nos. 4, 13, 17, 19, 21) all contain, with the exception of No. 13, the support component. Moreover, among these best catalysts, Mo as a main components as well as Sn as an minor component are present frequently. With the exception of Fe as a doping component, however, all employed catalyst components are still represented in the best five catalysts of the first generation.

2. Catalyst generation

Step 6. The second generation of catalysts was obtained in that first the five catalysts Nos. 4, 19, 21, 13, and 17 with the highest oxygenate yield of the 30 (corresponding to 17 % of the first generation of catalysts) that were previously tested were selected (compare step (c) above).

Step 7. The compositions of 10 new catalysts of the second generation were obtained in that

a) of the main, minor, doping, and support components of the five best catalysts (Table 1: Nos. 4, 19, 21, 13 and 17) six new combinations of main, minor, doping, and support components are formed (compare step (d) above), in that, for example, for the composition of the catalyst No. 1 of the second generation (Table 2) first the catalyst No. 17 (in the following catalyst No._ = K.) was selected by means of ZG1-Best5 [by means of the numerical random-check generators G05DYF, G05DZF, G05CCF of the NAG Library (NAG FORTRAN Workstation Library, NAG Group Ltd., 1986) of the best five catalysts] and subsequently by means of ZG1 [by means of the numerical random-check generators G05DYF, G05DZF, G05CCF of the NAG Library (NAG FORTRAN Workstation Library, NAG Group Ltd., 1986)] the main component Bi of K.17. Subsequently, K.21 (Table 1) was selected by means of ZG1-Best5 and then by means of ZG1 the main component P of K.21. Subsequently, K.4 (table 1) was selected by ZG1-Best 5 and then by means of ZG1 the minor component Sn of K.4. Subsequently, K.21 was selected by means of ZG1-Best5 and then by means of ZG1 the auxiliary component B of K.21. Subsequently, K.14 (Table 1)

was selected by means ZG1-Best5 and then by means of ZG1 the trace component Fe of K.14. Subsequently, K.19 (Table 1) was selected by means of ZG1-Best5 and then by means of ZG1 the trace component Co of K.19. Subsequently, K.17 (Table 1) was

5   selected by ZG1-Best5 and then by means of ZG1 the trace and doping components Cs and Pd of K.17. The thus selected components were combined with the original molar amounts to a new catalysts composition. In analogy, K.2, 3, 6, 7, 8 of the second catalyst generation (Table 2) were obtained.

10   b) The molar components of the main, minor, and doping components of the two best catalyst with the highest oxygenate yield (Table 1, Nos. 4 and 19) according to the above step (d) are changed in that the components Mo, Nb, Sb, Sn, Co and Ga of K.4 of the first generation are selected by

15   means of ZG1 and the molar fractions of the selected components are stochastically changed by means of ZG2 [by means of the numerical random-check generators G05CAF, G05DZF, G05CCF of the NAG Library (NAG FORTRAN Workstation Library, NAG Group Ltd., 1986)]. Subsequently, the components

20   Mo, Bi, P, Sn, Co of K.19 of the first generation were selected by ZG1 and the molar fractions of the selected components were stochastically changed by means of ZG2. K.4 and K.5 of the second generation were obtained (Table 2). In analogy, K.9 and K.10 of the second generation were

25   obtained. The preparation of the resulting total of 10 new catalysts of the second generation is carried out in analogy to that of the first generation (step 2).

Step 8. With the process described in step 7, 10 new catalyst compositions were determined, prepared according to the

30   procedure (compare step 1), and then tested parallel under standard conditions as described in step 4 (compare above step (e)). The results are compiled in Table 2. These new catalysts contain frequently Mo as a main component and Sn as a minor component. Also, P as a main component and Co as a

35   doping component, which already occurred with greater frequency in the best catalysts of the first generation, are also frequently contained in the new catalysts of the second generation.

Third catalyst generation

Step 9. From the quantity of the first and second catalyst generation the five catalysts were selected again which had the highest yield of oxygen derivatives (compare above step (f)). These are the catalysts of Table 1: Nos. 4, 19, 21 and

5 of Table 2: Nos. 2, 3. With the 10 new catalysts of the second generation initially no higher yields than with the best catalysts of the first generation are obtained. However, the catalysts Nos. 2 and 3 of the second generation displace the catalysts Nos. 19 and 21 from the third and fourth rank

10 (see also Fig. 1).

Step 10. The composition of the 10 new catalysts to be produced of the third generation was obtained in that with the five catalysts selected in step 9 the same procedure as in step 7 was performed (see Table 3, compare above step

15 (g)). Accordingly, K.4 (Table 2) was selected with ZG1-Best5 and then by means of ZG1 the main component Nb of K.4 (Table 2). Subsequently, K.21 (Table 1) was selected by means of ZG1-Best5 and then by means of ZG1 the main component P of K.21 (Table 1). Subsequently, K.3 (Table 2) was selected by

20 means of ZG1-Best5 and then by means of ZG1 the trace component Fe of K.14. Subsequently, K.19 (Table 1) was selected by means of ZG1-Best5 and then by means of ZG1 the doping component Co of K.3 (Table 2). Subsequently, K.4 (Table 1) was selected by means of ZG1-Best5 and then by

25 means of ZG1 the doping component Ga of K.4. Subsequently, K.2 (Table 2) was selected by means of ZG1-Best5 then by means of ZG1 the support component of K.2 (Table 2). The thus selected components were combined with their original molar fractions to a new catalyst composition. After the

30 combination, the molar fraction of the main component Nb was stochastically changed by means of ZG3 [by means of the numerical random-check generators G05CAF and G05CCF of the NAG Library (NAG FORTRAN Workstation Library, NAG Group Ltd., 1986)]. In analogy, K.2, 3, 6, 7, and 8 of the third catalyst

35 generation (Table 3) were obtained.

b) The same procedure as in portion b) of step 7 was carried out.

K.4 and K.5 of the third generation were obtained (Table 3). In analogy, K.9 and 10 of the third generation were obtained.

The preparation of the resulting total of 10 new catalysts of the third generation was carried out as in the first and second generation (steps 2 and 7).

Step 11. The 10 new catalysts of the third catalyst generation were prepared according to procedure (compare step 1) and tested parallel under standard conditions as in step 4 (compare above step (h)). Among these 10 new catalysts there are now two (Nos. 4 and 9) with which the previously highest yields are surpassed. Accordingly, the catalysts Nos. 4 and 19 (Table 1) are displaced from the first and second rank (compare Fig. 1).

Step 12. The selection of catalyst compositions of the following generations (the n-th generation) was carried out in analogy to the steps 6 - 8, respectively, 9 - 11 in that, respectively, the five best catalysts of all already tested catalyst generations were selected and used for the determination of the composition of the 10 new catalysts of the n-th catalyst generation (compare above steps (i), (j), (k)).

Result:

When the compositions of the five best catalysts of the first through third catalyst generation are compared, it is apparent that all catalysts contain Mo, Sn, Co, and the support component. The qualitative compositions of the three best catalysts are near identical. These catalysts contain all Mo, Nb, Sb, Sn, Co, Ga and the support component. The two best catalysts contain, in addition, also the doping components Cu and Pd. This underscores that the catalyst compositions with increasing generation number approximate one another, i.e., disruptive components are no longer considered during the course of optimization and the components of the catalysts with high oxygenate yield are more strongly taken into consideration upon determination of new catalysts compositions. On the basis of this evolutionary strategy, already in the third catalyst generation a 100 % higher oxygenate yield than in the first generation is obtained (Fig. 1).

Example 2

First, 20 catalysts (generation I), subsequently 10 catalysts (generations II and III), and subsequently further 10 catalysts (generation IV), based on 13 oxides which serve as primary catalyst components, are prepared and tested in the oxydative dehydrogenation of propane. The goal was to prepare propene from propane with a yield as high as possible and selectivity as high as possible by oxydative dehydrogenation. The course of the process comprised the following steps and resulted in the respectively denoted results.

1. Catalyst generation

Step 1. The components were selected from the oxides of the elements V, Mo, Mn, Fe, Zn, Ga, Ge, Nb, W, Co, Ni, Cd, In. The atom parts of the individual elements in the catalyst were varied between 0 and 1. Each catalyst contains three of the elements V, Mo, Mn, Fe, Zn, Ga, Ge, Nb, W, Co, Ni, Cd, In. The sum of all atom parts of these elements always results in 1.

Step 2. The catalyst compositions of the first generation are compiled in Table 4 which were obtained by means of ZG4 [numerical random-check generators G05DZF, G05CAF, G05DYF, G05CCF of the NAG Library (NAG FORTRAN Workstation Library, NAG Group Ltd., 1986)].

Step 3. The catalysts which were used for testing were obtained by the following manufacturing process:

Compounds (NH_4VO_3, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, Ga_2O_3, GeO_2, Nb_2O_5, H_2WO_4, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $In(NO_3)_3 \cdot H_2O$) of the elements named in step 1 were dissolved in water or suspended, mixed with one another, and the mixture evaporated. The resulting solid material was dried for 10 hrs. at 120 °C. and subsequently calcinated for 3 hrs. at 600 °C in air.

Table 4. Composition of Catalysts of the First Generation

Cat. No.	Composition	Cat. No.	Composition
1/1	$Fe_{0.79}Ga_{0.02}Nb_{0.19}O_x$	1/11	$V_{0.47}W_{0.19}Ni_{0.33}O_x$
1/2	$Mo_{0.44}Ni_{0.23}In_{0.33}O_x$	1/12	$Mn_{0.41}Ga_{0.51}Nb_{0.08}O_x$

1/3	$Zn_{0.70}Ge_{0.08}Co_{0.22}O_x$		1/13	$Mo_{0.45}Co_{0.22}In_{0.33}O_x$
1/4	$V_{0.33}Fe_{0.43}Cd_{0.24}O_x$		1/14	$Fe_{0.75}Ge_{0.05}W_{0.20}O_x$
1/5	$Ga_{0.01}Nb_{0.33}Ni_{0.66}O_x$		1/15	$V_{0.33}Mn_{0.43}Ni_{0.23}O_x$
1/6	$Mo_{0.33}Zn_{0.42}In_{0.25}O_x$		1/16	$Zn_{0.67}Nb_{0.1}Co_{0.23}O_x$
1/7	$Ge_{0.11}W_{0.33}Cd_{0.56}O_x$		1/17	$Mo_{0.33}Fe_{0.42}Cd_{0.25}O_x$
1/8	$V_{0.26}Mn_{0.33}Ga_{0.41}O_x$		1/18	$Ga_{0.01}W_{0.33}Ni_{0.66}O_x$
1/9	$Nb_{0.16}Co_{0.33}In_{0.51}O_x$		1/19	$Mn_{0.33}Zn_{0.41}In_{0.25}O_x$
1/10	$Mo_{0.42}Ge_{0.44}Fe_{0.53}O_x$		1/20	$Ge_{0.14}Co_{0.33}Cd_{0.53}O_x$

Step 4. The testing of the catalysts was carried out parallel in six quartz reactors (inner diameter 6 mm) which were introduced into a heatable and coolable fluidized sand bed for temperature control. The following standard experimental conditions were selected for the testing of the catalysts: T = 500 °C, $m_{catalyst}$ = 0.3 g, $C_3H_8/O_2/N_2$ = 2/1/2, V_{total} per reactor = was varied between 10 and 100 ml/min.(STP). The catalysts were used for the reaction and tested with respect to the propane conversion and propene selectivity under the aforementioned experimental conditions (compare step (b) above). The concentration of propane, propene, ethylene, methane, and the resulting oxygen derivatives as well as of CO and CO_2 was analyzed by means of a gaschromatograph.

Step 5. The results of the tests of the first generation of catalysts (propane conversion, propene selectivity, and propene yield) are represented in Table 5. Among the 20 tested catalyst significant differences in the yields resulted which are a product of conversion and selectivity. For catalysts (No. 1/4, 1/8, 1/10, 1/15) show the best results for the catalytic conversion.

Table 5. Catalytic Results of the First Generation

Cat.-No.	Composition	$X(C_3H_8)$ %	$S(C_3H_6)$ %	$Y(C_3H_6)$ %
1/1	$Fe_{0.79} Ga_{0.02} Nb_{0.19}$	10.7	17.7	1.9
1/2	$Mo_{0.44} Ni_{0.23} In_{0.33}$	11.8	14.3	1.7
1/3	$Zn_{0.70} Ge_{0.08} Co_{0.22}$	20.3	0.04	0.01
1/4	$V_{0.33} Fe_{0.43} Cd_{0.24}$	15.3	24.5	3.7
1/5	$Ga_{0.01} Nb_{0.33} Ni_{0.66}$	8.9	2.5	0.2
1/6	$Mo_{0.33} Zn_{0.42} In_{0.25}$	1.3	26.2	0.3
1/7	$Ge_{0.11} W_{0.33} Cd_{0.56}$	0.2	15.6	0.03
1/8	$V_{0.26} Mn_{0.33} Ga_{0.41}$	6.9	43.4	3.0
1/9	$Nb_{0.16} Co_{0.33} In_{0.51}$	15.2	12.1	1.8
1/10	$Mo_{0.42}Ge_{0.44} Fe_{0.53}$	6.3	35.1	2.2
1/11	$V_{0.47} W_{0.19} Ni_{0.33}$	44.6	2.3	1.0
1/12	$Mn_{0.41}Ga_{0.51} Nb_{0.08}$	13.1	12.7	1.7

1/13	$Mo_{0.45}\ Co_{0.22}\ In_{0.33}$	1.0	46.5	0.5
1/14	$Fe_{0.75}\ Ge_{0.05}\ W_{0.20}$	16.0	12.9	2.1
1/15	$V_{0.33}\ Mn_{0.43}\ Ni_{0.23}$	12.5	26.6	3.3
1/16	$Zn_{0.67}\ Nb_{0.1}\ Co_{0.23}$	15.2	0.3	0.05
1/17	$Mo_{0.33}\ Fe_{0.42}\ Cd_{0.25}$	2.1	7.7	0.2
1/18	$Ga_{0.01}\ W_{0.33}\ Ni_{0.66}$	23.6	3.3	0.8
1/19	$Mn_{0.33}\ Zn_{0.41}\ In_{0.25}$	15.7	9.5	1.5
1/20	$Ge_{0.14}\ Co_{0.33}\ Cd_{0.53}$	14.6	8.6	1.3

2. Catalyst generation

Step 6. The second generation of catalysts was obtained in that first the four catalysts (No. 4, 8, 10, 15) with the best catalytic behavior were selected and used for further modification.

Step 7. The compositions of the new catalysts 2/21 of the second generation were obtained in a similar way as described in step 7 of example 1, based on K.1/15 and the main component V, then K.1/8 and the main component Ga, then K.1/4 and the main component Cd, then K.1/10 and the minor component Ge. The thus selected components were combined with their original molar amounts to a new catalysts component. In analogy, the catalysts 2/22 to 2/30 of the second generation were obtained. The preparation of the resulting total of 10 new catalysts of the second generation was carried out as that of the first generation (step 2).

Step 8. With the procedure described in step 7, 10 new catalyst compositions were determined, produced according to the procedure (step 3), and then tested parallel under standard conditions as described in step 4 (compare step (e) above). The results are compiled in Table 6.

Table 6. Compositions and Catalytic Results of the Second Generation

Cat.-No.	Composition	$X(C_3H_8)$ %	$S(C_3H_6)$ %	$Y(C_3H_6)$ %
2/21	$V_{0.33}Ga_{0.40}Cd_{0.23}Ge_{0.04}O_x$	2.4	54.0	1.3
2/22	$V_{0.30}Fe_{0.48}Ni_{0.21}O_x$	26.1	1.4	0.4
2/23	$V_{0.30}Fe_{0.48}Cd_{0.22}O_x$	13.8	20.2	2.8
2/24	$V_{0.47}Mn_{0.22}Ga_{0.31}O_x$	17.0	37.0	6.3
2/25	$Mo_{0.45}Fe_{0.25}Ge_{0.29}O_x$	0.2	66.9	0.1
2/26	$Fe_{0.09}Ge_{0.33}Ni_{0.58}O_x$	16.7	1.8	0.3
2/27	$V_{0.26}Mo_{0.33}Fe_{0.41}O_x$	17.4	22.4	3.9
2/28	$Ga_{0.15}Ge_{0.33}Cd_{0.52}O_x$	2.7	6.2	0.2
2/29	$V_{0.43}Mn_{0.54}Fe_{0.03}O_x$	16.4	34.1	5.6
2/30	$V_{0.48}Ge_{0.19}Ni_{0.33}O_x$	43.1	0.4	0.2

3. Catalyst generation

Step 9. From the catalysts of the first and second catalyst generations, four catalysts with the best efficiency were again selected (Nos. 8, 24, 27, 29) (compare step (f) above) and used as a basis for further steps.

Step 10. The composition of 10 new catalysts to be produced of the third generation was obtained in that the same procedure as in step 7 or in step 10 of example 1 was carried out with the four catalysts selected in step 9 (see Table 6, compare step (g) above), based on K.2/19 and the main component V, then K.2/27 and the main component Mo, then K.2/24 and the main component Mn. The thus selected components were combined with their original molar amounts to a new catalyst composition. In analogy, the catalysts 3/52 to 3/60 of the third generation were obtained (Table 7). The preparation of the overall resulting 10 new catalysts of the third generation was carried out in analogy to that of the first and second generations (step 2 and 7).

Step 11. The 10 new catalysts of the third catalyst generation were prepared according to procedure (compare step 3) and tested parallel under standard conditions as described in step 4 (compare step (h) above).

Table 7. Compositions and Catalytic Results of the Third Generation

Cat.-No.	Compositions	$X(C_3H_8)/\%$	$S(C_3H_6)/\%$	$Y(C_3H_6)/\%$
3/51	$V_{0.32} Mo_{0.41} Mn_{0.27}$	13.6	28.4	3.9
3/52	$V_{0.26} Mn_{0.33} Ga_{0.41}$	20.4	29.9	6.1
3/53	$V_{0.20} Mn_{0.17} Fe_{0.32} Ga_{0.32}$	19.7	39.0	7.7
3/54	$V_{0.47} Mn_{0.13} Ga_{0.38}$	19.8	31.9	6.3
3/55	$V_{0.37} Mn_{0.22} Fe_{0.41}$	19.2	31.5	6.0
3/56	$Mn_{0.15} Fe_{0.33} Ga_{0.52}$	13.9	6.7	0.9
3/57	$V_{0.43} Mo_{0.54} Mn_{0.03}$	14.8	33.8	5.0
3/58	$Mo_{0.48} Fe_{0.18} Ga_{0.33}$	2.2	59.8	1.3
3/59	$V_{0.42} Mo_{0.52} Mn_{0.07}$	17.6	28.8	5.1
3/60	$V_{0.46} Fe_{0.21} Ga_{0.33}$	17.4	33.5	5.8

4. Catalyst generation

Step 12. Four catalysts with the best efficiency were again selected from the catalysts of the first through third catalyst generations (No. 24, 53, 54, 55) (compare step (f) above) and used as a basis for the new catalysts of the fourth generation.

Step 13. The composition of 10 new catalysts to be prepared of the fourth generation was obtained in that with the four catalysts selected in step 12 the same process as in step 7 was carried out (see Table 6, compare step (g) above).

Step 14. The 10 new catalysts of the third catalyst generation were prepared according to procedure (compare step 3) and tested parallel under standard conditions as in step 4 (compare step (h) above).

According to Fig. 2, a significant increase of the propene yield was obtained already in the fourth generation.

Tabelle 8. Compositions and Results of the Fourth Generation

Cat.-No.	Compositions	$X(C_3H_8)$ %	$S(C_3H_6)$ %	$Y(C_3H_6)$ %
4/71	$V_{0.49}$ $Mn_{0.13}$ $Ga_{0.38}$	18.6	39.4	7.3
4/72	$V_{0.53}$ $Mn_{0.14}$ $Fe_{0.34}$	18.8	27.1	5.1
4/73	$V_{0.32}$ $Fe_{0.27}$ $Ga_{0.27}$	21.7	32.9	7.1
4/74	$V_{0.19}$ $Mn_{0.24}$ $Fe_{0.32}$ $Ga_{0.25}$	22.3	35.9	8.0
4/75	$V_{0.06}$ $Mn_{0.02}$ $Ga_{0.92}$	22.2	34.6	7.7
4/76	$Mn_{0.5}$ $Fe_{0.16}$ $Ga_{0.33}$	21.6	32.6	7.0
4/77	$V_{0.42}$ $Mn_{0.53}$ $Ga_{0.04}$	9.7	34.1	3.3
4/78	$V_{0.47}$ $Fe_{0.19}$ $Ga_{0.33}$	22.2	33.0	7.3
4/79	$V_{0.41}$ $Mn_{0.51}$ $Fe_{0.08}$	12.6	22.1	2.8
4/80	$V_{0.45}$ $Fe_{0.22}$ $Ga_{0.33}$	20.9	33.4	7.0

Table 1

First Catalyst Generation

No.	Composition mole-%																support weight -%	Pd weight -%	Yield of an C3-Oxygenates mole-%	Rank among the 5 best Catalyst - Generations		
	Main component					Minor component				Doping component										1	2	3
	V	Mo	Nb	Bi	P	Mn	Sb	Sn	B	Fe	Co	Cs	Ag	Cu	Ga	In						
1	13,75	6,75	0	0	0	16,84	9,83	0	2,83	0,344	0	0	0	0	0	0	50	0,0001	0,000			
2	40,48	22,76	0	5,05	30,57	0	0	0	0	0	0	0	0	0	0	1,137	50	0,0001	0,000			
3	0	20,85	2,97	0	28,73	0	10,85	23,60	0	0	0	0	0,449	0	0	0	0	0,0001	0,034			
4	0	15,12	4,96	0	0	0	19,60	9,44	0	0	0,887	0	0	0	0,340	0	50	0	0,430	1.	1.	3.
5	8,59	0	0	0	0	23,87	13,26	0	2,65	0,448	0	0,707	0,173	0	0	0,595	50	0,0001	0,005			
6	11,04	38,88	0	19,56	0,230	0	0	0	28,07	0,761	0	1,63	0	0	0	0	0	0	0,000			
7	0	0	29,53	12,88	0	36,86	20,22	0	0	0	0	0	0	0	0,372	0	0	0	0,025			
8	11,96	38,26	0	0	20,00	0	1,74	28,04	0	0,463	0	0,748	0,843	0	0	0	50	0,0001	0,007			
9	0	9,09	22,49	0	0	0	13,19	3,88	0	0	0	0,305	0,262	0	0,763	0,610	0	0	0,039			
10	10,14	0	1,54	13,93	0	0	5,33	0	17,72	0,218	0	0,410	0	0,467	0	0	50	0,0001	0,024			
11	0	0	0	6,09	0	0	29,09	0	13,12	1,232	0	0,398	0,987	0	0	0,427	50	0,0001	0,011			
12	0	0	0	18,37	6,77	0	0	0	23,48	0,287	0	0,548	0,607	0	0	0,986	50	0,0001	0,030			
13	0	6,69	34,53	0	0	0	0	15,20	43,04	0	0	0	0	0	0	0	0	0,0001	0,082	4.		
14	0	11,33	4,54	0	14,33	7,53	0,73	0	10,53	0,321	0	0,668	0,226	0	0	0,343	50	0	0,016			
15	0	20,09	11,40	0	0	0	0	2,70	15,23	0	0	0,582	0	0	0	0	50	0,0001	0,053			
16	10,37	1,67	0	14,20	5,50	0	0	18,04	0	0	0,222	0	0	0,435	0,166	0	50	0,0001	0,045			
17	8,56	2,90	0	11,06	5,40	0	0	13,55	7,89	0	0	0,198	0	0	0	0	50	0,0001	0,077	5.		
18	14,11	0	5,89	17,74	0	0	9,51	1,28	0	0,318	0	0,495	0,640	0	0	0,340	50	0	0,011			
19	0	9,11	0	23,40	13,48	0	0	3,56	0	0	0,466	0,318	0	0,452	0,700	0	0	0,0001	0,215	2.	2.	4.
20	27,10	15,00	0	2,90	20,33	0	0	8,23	25,66	0	0	0,393	0	0	0	0	50	0,0001	0,015	3.		5.
21	0	0	0	0	18,58	5,69	0	0	24,25	0	1,069	0	0	0	0	0	0	0	0,085			
22	0	0	0,187	12,82	0	37,00	20,21	0	0	0	0,363	0	0,939	0	0,346	0	0	0,0001	0,001			
23	0	0	29,61	39,59	0	3,10	55,66	0	0	0	0	1,652	0	0	0	0	0	0	0,001			
24	20,70	5,98	0	27,18	12,47	33,67	0	18,06	0	1,723	0	0	0	0	0,474	0	0	0	0,005			
25	0	0	0	31,94	7,13	0	42,87	0,94	28,17	0	0	0,801	0	0	0	0	0	0,0001	0,018			
26	11,51	0	38,74	19,84	0	0	0	13,02	0	0	0	0	0	0	0	0,208	50	0,0001	0,002			
27	6,69	17,04	0	9,85	2,67	0	0	1,77	21,00	0	0,531	0,328	0	0,454	0,691	0	0	0,0001	0,014			
28	22,58	9,24	0	0	28,46	15,12	0	15,17	0	0	0,659	0	0	0	0,240	0	50	0,0001	0,000			
29	0	0	19,95	0	11,41	0	2,87	0	0	0	0	0,597	0	0	0	0	0	0	0,004			
30	29,36	11,64	0	37,17	19,45	0	0	1,73	0	0	0,649	0	0	0	1,001	0	0	0	0,002			

Table 2

Second Catalyst Generation

No.	Main component				Minor component					Doping component							support weight-%	Pd weight-%	Yield of an C_3-Oxygenates mole-%	Rank among the 5 best Catalyst-Generations	
	V	Mo	Nb	Bi	P	Mn	Sb	Sn	B	Fe	Co	Cs	Ag	Cu	Ga	In				2	3
1	0	0	0	8,54	14,34	0	0	7,28	18,72	0,83	0,825	0,303	0	0	0	0	50	0,0001	0,037		
2	0	10,82	0	0	22,07	0	0	16,10	0	0,55	0,553	0,467	0	0	0	0	50	0,0001	0,184	3.	5.
3	0	15,47	0	0	19,01	0	0	13,87	0	0	0,908	0,402	0	0	0,325	0	50	0	0,161	4.	
4	0	2,87	15,14	0	0	0	26,50	4,22	0	0	0,738	0	0	0	0,536	0	50	0,0001	0,001		
5	0	11,79	0	11,48	1,35	0	0	24,43	0	0	0,952	0	0	0	0	0	50	0,0001	0,024		
6	0	4,37	3,24	7,22	12,13	0	12,80	9,93	0	0	0,300	0	0	0	0	0	50	0,0001	0,020		
7	0	0	0	0	26,54	0	0	21,71	0	0	1,270	0	0	0	4,810	0	50	0,0001	0,024		
8	6,42	6,82	0	0	13,92	4,27	0	11,39	5,91	0	0,670	0,150	0	0,330	0,120	0	50	0,0001	0,000		
9	0	4,04	9,23	0	0	0	20,15	13,75	0	0	2,090	0	0	0	0,740	0	50	0,0001	0,003		
10	0	3,09	0	26,10	5,85	0	0	13,69	0	0	1,270	0	0	0	0	0	50	0,0001	0,000		

Composition mole-%

Table 3

Third Catalyst Generation

No.	Composition mole-%																support weight -%	Pd weight -%	Yield of an C₃-Oxygenates mole-%	Rank among the 5 best Catalyst - Generations
	Main component					Minor component				Doping component										
	V	Mo	Nb	Bi	P	Mn	Sb	Sn	B	Fe	Co	Cs	Ag	Cu	Ga	In				
1	0	0	31,78	0	17,10	0	0	0	0	0	0,82	0	0	0	0,31	0	50	0,0001	0,006	
2	0	6,34	24,05	0	12,94	0	0	0	5,50	0	0,62	0,14	0	0,30	0,12	0	50	0,0001	0,096	
3	0	6,40	14,62	9,90	0	0	0	0	18,22	0	0,38	0,23	0	0,12	0,07	0	50	0	0,010	
4	0	34,61	0,87	0	0	0	5,37	8,28	0	0	0,43	0	0	0,07	0,45	0	50	0,0001	0,821	2.
5	0	19,45	0	13,27	2,67	0	0	13,64	0	0	0,96	0	0	0,45	0	0	50	0,0001	0,035	
6	0	5,94	4,40	9,82	0	0	17,40	12,03	0	0	0,41	0	0	0	0	0	50	0,0001	0,000	
7	0	0	7,47	0	20,29	0	0	20,40	0	0	1,34	0	0	0	0,51	0	50	0,0001	0,050	
8	0	8,70	4,74	0	12,88	0	0	14,53	7,54	0	0,85	0,19	0	0,51	0,16	0	50	0	0,161	1.
9	0	17,74	4,63	0	0	0	15,86	10,15	0	0	0,43	0	0	0,16	1,20	0	50	0,0001	0,965	
10	0	1,66	0	31,55	7,22	0	0	9,00	0	0	0,56	0	0	1,20	0	0	50	0,0001	0,063	

CLAIMS

1. A method for preparing active or selective solid
   catalysts of inorganic or organometallic materials or
   mixtures thereof by selecting a certain number of solid
   catalysts of different chemical composition or different
   weight composition or different chemical and different
   weight composition and determination of essential
   catalyst properties,
   comprising
   arbitrarily or randomly newly structuring by means of
   stochastic methods the individual catalyst components or
   amounts of mass of the catalyst components or the
   catalyst components and amounts of mass in the best
   catalysts of the first generation with respect to
   activity or selectivity or activity and selectivity for
   a certain catalytic reaction,
   determining the activity or selectivity or activity and
   selectivity of the obtained catalysts of the second
   generation,
   again arbitrarily or randomly newly structuring by means
   of stochastic methods the individual catalyst components
   or amounts of mass of the catalyst components or the
   catalyst components and amounts of mass of a portion of
   the best catalysts of the second generation,
   determining the activity or selectivity or activity and
   selectivity of the obtained catalysts of the third
   generation, and continuing these steps of new
   structuring of the best catalysts of all generations and
   the property determination up to obtaining one or more
   catalysts with the desired properties for the specific
   catalytic reaction.

2. The method for preparing active or selective solid
   catalysts according to claim 1, wherein

   (a) for a catalytic reaction a number n_1 of solid
       catalysts of the elements of the periodic table of

the elements (PTE) in the form of compounds of the formula (I)

$$\left(A^1_{a_1}..A^i_{a_i}\right) - \left(B^1_{b_1}..B^j_{b_j}\right) - \left(D^1_{d_1}..D^k_{d_k}\right) - \left(T^1_{t_1}..T^l_{t_l}\right) - O_p \qquad (I)$$

are prepared, wherein A^1 .. A^i is a quantity i of different main components which are selected from the elements of the PTE, except trans uranium and noble gas elements, and the number i is between 1 and 10,

B^1 .. B^j is a quantity j of different minor components selected from the group of the elements Li, Na, Ka, Mg, Ca, Sr, Ba, Y, La, Ti, Zr, V, Nb, Cr, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, B, Al, Ga, In, C, Si, Sn, Pb, N, P, As, Sb, Bi, S, Se, Te, F, Cl, Ce and Nd, and the number j is between 1 and 10,

D^1 .. D^k is a quantity k of different doping elements which are selected from the group of the elements Li, Na, Ka, Mg, Ca, Sr, Ba, Y, La, Ti, Zr, V, Nb, Cr, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, B, Al, Ga, In, Si, Sn, Pb, N, P, As, Sb, Bi, S, Se, Te, F, Cl, Ce and Nd and the number k is between 1 and 10,

T^1 .. T^l is a quantity l of different support components which are comprised of oxides, carbonates, carbides, nitrides, borides of the elements Mg, Ca, Sr, Ba, La, Zr, Ce, Al, Si or a mixed phase of two or more thereof, and the number l is between 1 and 10, and O is oxygen,

$a_1..a_i$ are identical or different mole fractions of 0 to 100 mole-% with the provision that the mole fractions $a_1..a_i$ cannot all at the same time be 0,

b_1 .. b_j are mole fractions of 0 to 90 mole-%,

d_1 .. d_k are mole fractions of 0 to 10 mole-%,

t_1 .. t_l are mole fractions of 0 bis 99.99 mole-%,

p is a mole fraction of 0 to 75 mole-%, wherein the sum of all mole fractions $a_i + b_j + d_k + t_l$ may be not greater than 100 %, and

the number n_1 of catalysts with different quantitate composition or different chemical composition or

different weight and chemical compositions is in the range of 5 to 100,000;

(b) the activity or selectivity or activity and selectivity of the n_1 solid catalysts prepared according to (a) of the first generation is determined experimentally for a catalytic reaction in a reactor or in several reactors switched parallel;

(c) a number of 1 - 50 % is selected as number n_2 from the number n_1 of the catalysts of the first generation having the highest activities for a specific reaction or highest selectivities for the desired product or product mixture of the catalytic reaction or activity and selectivity;

(d) the catalyst components contained in the number n_2 of the catalysts with a pre-set probability W, which results for each of the components A^1 .. A^i, B^1 .. B^j, D^1 .. D^k and T^1 .. T^l from the corresponding equations

$$W_A = \frac{1}{i \cdot n_2} \cdot 100\%, \; W_B = \frac{1}{j \cdot n_2} \cdot 100\%, \; W_D = \frac{1}{k \cdot n_2} \cdot 100\%, \; W_T = \frac{1}{l \cdot n_2} \cdot 100\%$$

are exchanged between two catalysts selected from the number n_2 with a probability of $W_{cat} = \frac{1}{n_2} \cdot 100\%$ or

that the amount of mass a_1 .. a_i, b_1 .. b_j, d_1 .. d_k and t_1 .. t_l of the catalyst components A^1 .. A^i, B^1 .. B^j, D^1 .. D^k and T^1 .. T^l for some of the catalysts selected with a probability of $W_{cat} = \frac{1}{n_2} \cdot 100\%$

are varied in that new values for the mole fractions a_1 .. a_i, b_1 .. b_j, d_1 .. d_k and t_1 .. t_l are determined within the limits defined under (a); or that exchange and variation are performed; in this way new catalysts of the general formula (I) with the meaning of A, B, D, T, a, b, d, and t and p

as defined under (a) are produced in a number y_2 which form the catalysts of the second generation;

(e) the activities or selectivities or activities and selectivities of the y_2 solid catalysts of the second generation are determined experimentally for the same specific reaction as in (b) in one or more reactors;

(f) a number of the n_3 catalysts of the second generation, having the highest activities for a specific reaction or highest selectivities for the desired product and product mixture or the activities and selectivities of all solid catalysts of the first and second generation, is selected, wherein the number n_3 is 1 to 50 % of the number n_1;

(g) the catalyst components contained in the number n_3 of the catalysts with a pre-set probability W, which results for each of the components A^1 .. A^i, B^1 .. B^j, D^1 .. D^k and T^1 .. T^l from the corresponding equations

$$W_A = \frac{1}{i \cdot n_3} \cdot 100\%, W_B = \frac{1}{j \cdot n_3} \cdot 100\%, W_D = \frac{1}{k \cdot n_3} \cdot 100\%, W_T = \frac{1}{l \cdot n_3} \cdot 100\%$$

are exchanged between two catalysts selected from the number n_3 with a probability of $W_{cat} = \frac{1}{n_3} \cdot 100\%$ or that the amount of mass a_1 .. a_i, b_1 .. b_j, d_1 .. d_k and t_1 .. t_l of the catalyst components A^1 .. A^i, B^1 .. B^j, D^1 .. D^k and T^1 .. T^l for some of the catalysts selected with a probability of $W_{cat} = \frac{1}{n_3} \cdot 100\%$ are varied in that new values for the mole fractions a_1 .. a_i, b_1 .. b_j, d_1 .. d_k and t_1 .. t_l are determined within the limits defined under (a) or exchange and variation are performed;

in this way new catalysts of the general formula (I) with the meaning of A, B, D, T, a, b, d and t and p

as defined under (a) are produced in a number y_3 which form the catalysts of the third generation;

(h) the activity or selectivity or activity and selectivity is of the y_3 new solid catalysts of the third generation prepared according to (g) is determined experimentally for the same specific reaction as in (b) in one or more reactors;

(i) a number of n_{n+1} solid catalysts of the n-th generation, having the highest activities for a catalytic conversion or the highest selectivities for the desired product and product mixture or the highest activity and selectivity of all solid catalysts of the first to n-th generation, is selected, wherein the number n_{n+1} is 1 to 50 % of the number n_1;

(j) the catalyst components contained in the number n_{n+1} of the catalysts with a pre-set probability W, which results for each of the components $A^1 .. A^i$, $B^1 .. B^j$, $D^1 .. D^k$ and $T^1 .. T^l$ from the corresponding equations

$$W_A = \frac{1}{i \cdot n_{n+1}} \cdot 100\%, W_B = \frac{1}{j \cdot n_{n+1}} \cdot 100\%, W_D = \frac{1}{k \cdot n_{n+1}} \cdot 100\%, W_T = \frac{1}{l \cdot n_{n+1}} \cdot 100\%$$

are exchanged between two catalysts selected from the number n_{n+1} with a probability of $W_{cat} = \frac{1}{n_{n+1}} \cdot 100\%$

or that the amount of mass $a_1 .. a_i$, $b_1 .. b_j$, $d_1 .. d_k$ and $t_1 .. t_l$ of the catalyst components $A^1 .. A^i$, $B^1 .. B^j$, $D^1 .. D^k$ and $T^1 .. T^l$ for some of the catalysts selected with a probability of $W_{cat} = \frac{1}{n_{n+1}} \cdot 100\%$

are varied in that new values for the mole fractions $a_1 .. a_i$, $b_1 .. b_j$, $d_1 .. d_k$ and $t_1 .. t_l$ are determined within the limits defined under (a), or that exchange and variation are performed;

in this way new catalysts of the general formula (I) with the meaning of A, B, D, T, a, b, d and t and p as defined under (a) are produced in a number y_{n+1} which form the catalysts of the (n+1)-th generation;

(k) the activity or selectivity or activity and selectivity of the y_{n+1} solid catalysts of the (n+1)-th generation prepared according to (g) is determined experimentally for the same specific reaction as in (b) in one or more reactors;

(l) the selection according to the steps (c) + (f) + (i), the preparation of a new catalyst generation according to the steps (d), (g), (j), and the activity/selectivity determination according to the steps (e) + (h) + (k) is continued up to obtaining a catalyst generation in which the activity or selectivity or activity and selectivity relative to the previous generations as an arithmetic mean is not increased or no longer significantly increased.

3. The method according to claim 2, wherein the exchange of the catalysts or the variation of the amount of mass or exchange and variation in the portions (d), (g), and (j) are carried out by means of a numerical random-check generator.

4. The method according to claim 3, wherein the program codes G05CAF, G05DYF, G05DZF and G05CCF of the NAG Library (NAG FORTRAN Workstation Library, NAG Group Ltd., 1986) of a numerical random-check generator are used.

5. The method according to claim 2(a), wherein the quantity n_1 is in the range of 5 to 100 for catalysts which are different with regard to their weight composition or chemical composition or weight and chemical composition.

6. The method according to claim 2, wherein the selection number n_2, n_3, or n_{n+1} is 5 to 30 % of the quantity n_1.

7. The method according to claim 2, wherein the main components are selected from the group comprised of Mg, Ca, Sr, Ba, Y, La, Ti, Zr, V, Nb, Cr, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, B, Al, Ga, In, C, Si, Sn, Pb, N, P, As, Sb, Bi, S, Se, Te, F, Cl, Ce und Nd.

8. The method according to claim 2, wherein the mole fractions b_1 .. b_j are from 0 to 50 mole-%.

9. The method according to claim 2, wherein the preparation of the catalyst mixtures is carried out by mixing salt solutions of the elements of the components A^1 .. A^i, B^1 .. B^j, D^1 .. D^k and T^1 .. T^l and subsequent thermal treatment in the presence of a reactive or inert gas phase (tempering) or by common precipitation of sparingly soluble compounds and subsequent tempering or by loading of the support component T^1 .. T^l with salt solutions or gaseous compounds of the components A^1 .. A^i, B^1 .. B^j, D^1 .. D^k and subsequent tempering, wherein the employed salts are nitrates, sulfates, phosphates, carbonates, halogenides, oxalates, carboxylates, or mixtures thereof or carbonyl compounds or as acetyl acetonates.

10. The method according to claim 2, wherein the catalytic reaction is carried out with liquid, evaporated, or gaseous reactants.

11. The method according to claim 2, characterized in that the reactants for the catalytic reaction is supplied to several reactors and the product stream exiting the reactors is separately analyzed for each individual reactor.

12. The method according to claim 11, wherein for performing the catalytic reaction 5 to 1,000 reactors comprised of spaces with catalytically active material arranged therein are arranged parallel to one another or arranged in

arrays, wherein the diameter of these spaces is 100 μm to 10 mm and the lengths are 1 mm to 100 mm.

13. The method according to claim 11, wherein, for a preset reactor length, the throughput of reactants is selected such that the desired degree of conversion is reached.

14. The method according to claim 11, wherein a monolithic block with several parallel channels, which can be closed selectively at the inlet or outlet side individually or in larger number also during the catalytic reaction, or a porous module having channels extending preferably parallel to the flow direction of the reaction mixture which channels can be selectively individually or in large number closed at the inlet or outlet side also during the catalytic reaction, is used as the reactor.

15. The method according to claim 1, wherein the reactants for the catalytic reaction are supplied to the reactors according to claim 11, 12, and 13, and wherein the composition of the product streams exiting the reactors is analyzed by a measuring sensor, wherein the measuring sensor is guided two-dimensionally across the exit cross-section of all reactors or the reactors are moved two-dimensionally relative to the measuring sensor and the portion of the product streams received by the measuring sensor is supplied to the analytical device.
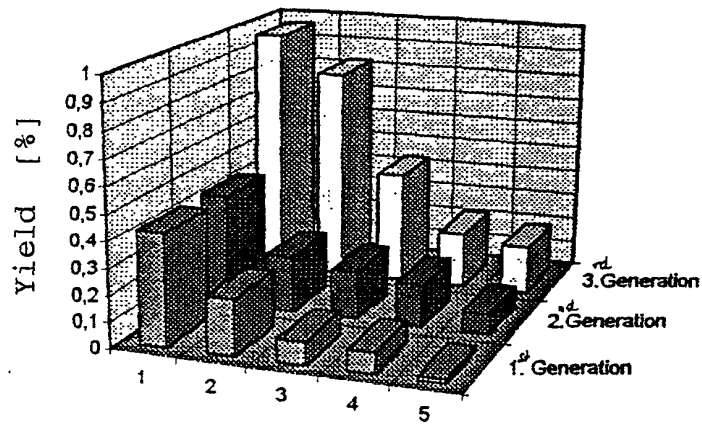
Fig. 1
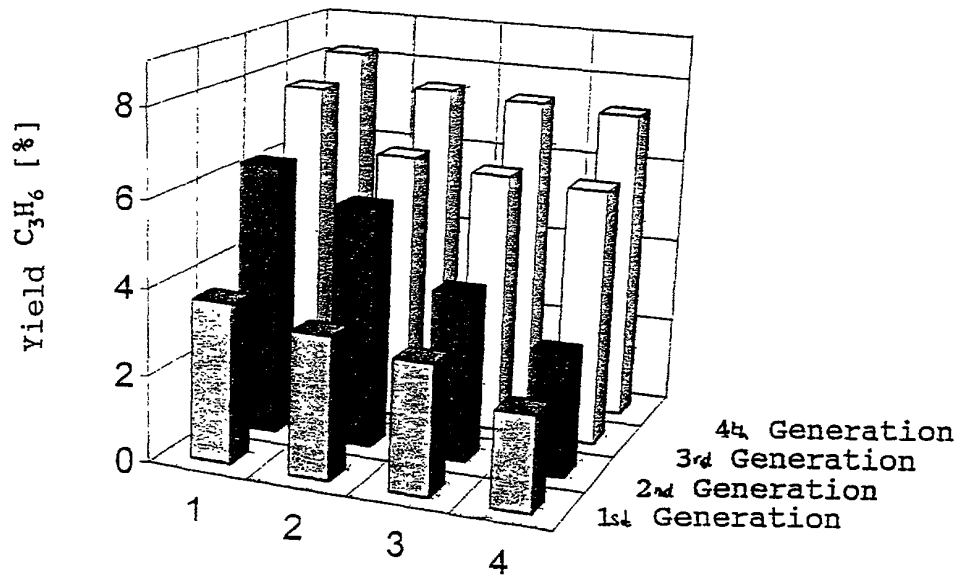
Fig. 2

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY

ATTORNEY'S DOCKET NUMBER

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Method for producing active and/or selective solid catalysts

from inorganic or organometallic materials

the specification of which (check only one item below):

☐ is attached hereto.

☐ was filed as United States application

Serial No. _____

on _____.

and was amended

on _____ (if applicable).

☒ was filed as PCT international application

Number ——— PCT/DE99/02956 ———————

on September 10, 1999 _____.

and was amended under PCT Article 19

on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowlege the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119:

COUNTRY	APPLICATION NUMBER	DATE OF FILING (day, month year)	PRIORITY CLAIMED UNDER 35 USC 119	
Fed. Rep. of Germany	198 43 242.9	11/09/98	☒ YES	☐ NO
			☐ YES	☐ NO
			☐ YES	☐ NO
			☐ YES	☐ NO
			☐ YES	☐ NO

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (Includes Reference to PCT International Applications)	ATTORNEY'S DOCKET NUMBER

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclose in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:

PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120:

U.S. APPLICATIONS		STATUS *(Check One)*		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED

PCT APPLICATIONS DESIGNATING THE U.S.					
PCT APPLICATION NO.	PCT FILING DATE	U.S. SERIAL NUMBERS ASSIGNED *(if any)*			

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. *(List name and registration numbers):*

(4) ALLISON C. COLLARD, Registration No. 22,532;
EDWARD R. FREEDMAN, Registration No. 26,048;
ELIZABETH COLLARD RICHTER, Registration No. 35,103;
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

SIGNATURE OF INVENTOR 201 *D. Wolf*	SIGNATURE OF INVENTOR 202 *O. Gerlach*	
DATE January 26, 2001	DATE January 30, 2001	

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (Includes Reference to PCT International Applications)	ATTORNEY'S DOCKET NUMBER

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclose in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:

PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120:

U.S. APPLICATIONS		STATUS (Check One)		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED

PCT APPLICATIONS DESIGNATING THE U.S.

PCT APPLICATION NO.	PCT FILING DATE	U.S. SERIAL NUMBERS ASSIGNED (if any)			

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (List name and registration numbers):

ALLISON C. COLLARD, Registration No. 22,532;
EDWARD R. FREEDMAN, Registration No. 26,048;
ELIZABETH COLLARD RICHTER, Registration No. 35,103;
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

SIGNATURE OF INVENTOR 203	SIGNATURE OF INVENTOR 204	
DATE Jan. 31, 2001	DATE Jan. 25, 2001	

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (Includes Reference to PCT International Applications)	ATTORNEY'S DOCKET NUMBER

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclose in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:

PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120:

U.S. APPLICATIONS		STATUS (Check One)		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED

PCT APPLICATIONS DESIGNATING THE U.S.				
PCT APPLICATION NO.	PCT FILING DATE	U.S. SERIAL NUMBERS ASSIGNED (if any)		

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (List name and registration numbers):

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FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY

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SIGNATURE OF INVENTOR 201	SIGNATURE OF INVENTOR 202	
DATE Jan 26, 2001	DATE	